^{15}N Nuclear Magnetic Resonance Spectra of Octaethylporphyrin

By KEIICHI KAWANO, YUKIHIRO OZAKI, and YOSHIMASA KYOGOKU*
(*Institute for Protein Research, Osaka University, Suita, Osaka* 565, *Japan*)
and HISANOBU OGOSHI, HIROSHI SUGIMOTO, and ZEN-ICHI YOSHIDA
(*Department of Synthetic Chemistry, Kyoto University, Yoshida, Sakyo-ku, Kyoto* 606, *Japan*)

Summary ^{15}N and ^{1}H n.m.r. spectra of 97% [^{15}N]octaethylporphyrin have clearly indicated that the two central hydrogens exchange between the four nitrogen atoms at and above room temperatures.

FROM the analyses of ^{1}H and ^{13}C n.m.r. spectra of alkyl-substituted porphyrins and tetraphenylporphyrin it has been claimed that two central hydrogens exchange sufficiently rapidly for averaging the chemical shift differences at room temperature.[1] In the present investigation ^{15}N and ^{1}H n.m.r. spectra of 97% [^{15}N]-enriched octaethylporphyrin, [$^{15}N_4$]-OEPH$_2$, were observed and these verified the above argument. In addition the ^{15}N n.m.r. spectra of metal complexes of this porphyrin with Mg, Zn, and Cd were obtained.

The ^{15}N label was incorporated during the Knorr synthesis of ethyl 3-acetyl-4-ethyl-2-methylpyrrole-5-carboxylate using Na$^{15}NO_2$ (97·3%).[2] Proton-decoupled ^{15}N n.m.r. spectra at 10·09 MHz were recorded on a JEOL–PFT-100 pulse Fourier transform n.m.r. system locked on deuterium. Chemical shifts were measured relative to external NH$_4$-$^{15}NO_3$ in $(CD_3)_2SO$.

In the Figure only a sharp signal with a negative n.O.e. (nuclear Overhauser enhancement) is seen at 90 °C, indicating that two central hydrogens exchange on the four nitrogen atoms rapidly enough to maintain four-fold symmetry on the n.m.r. time scale. At lower temperatures, however, two distinct resonances are observed. The position of the upper-field resonance (249·1 p.p.m.) is comparable with that of di-protonated [$^{15}N_4$]-OEPH$_4^{2+}$ in trifluoroacetic acid (253·7 p.p.m.), and the lower resonance position (139·7 p.p.m.) is closer to that of N-1 of [$^{15}N_3$]riboflavin (178·0 p.p.m.).[3] Thus the two central hydrogens seem to be fixed on two of the nitrogen atoms at lower temperatures giving the upper-field resonance. The negative n.O.e. of the lower-field signal of the proton-free nitrogens is probably due to exchange being slow on the chemical shift time scale but fast on the T_1 time scale, and is partly due to their proximity to the fixed hydrogens.[4] The two resonance signals coalesced around room temperature and the activation energy, $\Delta G^‡$, of the hydrogen exchange was calculated to be *ca.* 12 kcal mol.$^{-1}$

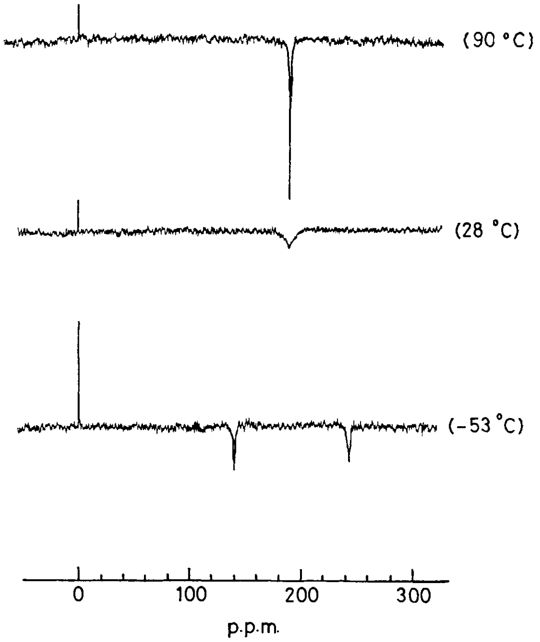

FIGURE. Temperature dependence of the proton-decoupled ^{15}N n.m.r. spectra of 97% [^{15}N]octaethylporphyrin, 0·019M in CDCl$_3$, 20k accumulations with 2 s intervals.

The resonance of the central protons at 100 MHz showed a similar temperature dependency; at and above room temperature they gave a singlet and at lower temperature a doublet, owing to coupling to ^{15}N. The coupling constant [$^1J(^{15}N\text{–}H) = 98$ Hz] is virtually identical with that reported for pheophytin a.[5]

The metal complexes of [$^{15}N_4$]octaethylporphyrin with Mg, Zn, and Cd ions gave single non-inverted signals at 180·4 (in CDCl$_3$), 179·2 (in CDCl$_3$ + C$_5$D$_5$N), and 173·1 (in C$_5$D$_5$N) p.p.m., respectively. Although it was difficult to obtain spectra with high signal to noise ratios because of low solubility of the samples and long relaxation times of the proton-free ^{15}N nuclei, the resonance positions were confirmed with INDOR by monitoring the methine proton resonances at 100 MHz.

In the ^1H n.m.r. spectrum the methine proton in metal-free [$^{15}N_4$]-OEPH$_2$ is shown to be coupled to two ^{15}N atoms, three bonds removed, leading to a triplet for the X part of the A$_2$X system [$^3J(^{15}N\text{–}H) = 4·7$ Hz]. On complexation with the metal ion additional couplings are observed as shoulders resulting from 'virtual coupling'[6] *via* the central metal ion. The spectra should be analysed as the X part of an A$_2$A$_2$'X system taking into account the couplings between the ^{15}N nuclei.

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